

## REMARKS

Applicants would like to thank Examiner Musser for the helpful and courteous interview held with Applicants' representatives, on March 27, 2003. At that time, the Examiner explained the basis of her rejection of the claims based on 35 U.S.C. § 112 2<sup>nd</sup> paragraph, and she was receptive to the idea of amending the claims demonstrating that the protective layer, Fp, was removable, and she suggested that this amendment would obviate this rejection. New claims 4-16 have been drafted with the Examiner's comments in mind, and are free of this rejection.

Additionally, Examiner recognized that defining the protective layer as being removable obviates the rejection of the claimed method under 35 U.S.C. § 103(a) in light of Sawamura et al. (EP 0878285A1) and Dornbusch et al. (U.S. Patent 4,883,697), as both references outline processes or products dealing with labels, not self-adhesive parts.

During the interview, the Examiner was interested in the fact that the current invention employed silicone resins, while the prior art references employed silicone rubbers. In addition, Applicants' representatives explained that Strickland et al. (U.S. Patent 5,983,527) did not disclose that "injection molding a substrate against an adhesive results in a better bond," as compared to attaching the substrate outside the mold.

As explained at the interview, the present invention is directed to a method for producing self-adhesive molded silicone parts that overcomes the problems associated with adhering a silicone part to its substrate by adhesive bonding or by overmolding. The process is distinguished over the prior art by the fact that the components used to make the self-adhesive stack are placed into the mold prior to adding the uncured silicone-resin. The prior art does not teach using a preformed self-adhesive stack. Furthermore, the prior art uses extruded silicone rubbers or silicone liquid-injection-molding rubber. It does not use silicone resin, nor does it place a preformed adhesive stack inside of a mold.

Applicants' claimed process for manufacturing a self-adhesive molded silicone part, comprises: placing into a half-mold (M1), comprising a hollow cavity (E<sub>1</sub>), an adhesive stack comprising a removable protective sheet (Fp), a first adhesive layer (Ce), an intermediate sheet (Fi), and a second adhesive layer (Cs); joining a second half-mold (M2), comprising a second hollow cavity (E<sub>2</sub>), with half-mold (M1) comprising said adhesive stack, wherein the cavities of the half-molds face one another; injecting a silicone resin (R) into the cavity produced by the joining of half-molds M1 and M2; curing the mold injected silicone resin; and demolding the resultant self-adhesive molded silicone part.

This claimed method has been rejected under 35 U.S.C. 103(a) as being unpatentable over Gerritsen (U.S. Patent 4,658,548), in view of Clark (U.S. Patent 4,351,686), Strickland et al. (U.S. Patent 5,983,527), and Sawamura et al. (EP 0878285A1).

Gerritsen applies a non-silicone-based double-sided adhesive to an extruded silicone rubber part outside of a mold. Clark applies a non-silicone based adhesive to a pretreated silicone rubber part outside of a mold. The pretreatment procedure comprises applying a toluene-diluted silicone-based adhesive to the silicone rubber part followed by drying by air or using a heat lamp. Strickland et al. prepares a non-silicone-based molded shoe sole without using a silicone-based adhesive. Strickland et al. either casts or extrudes a non-silicone-based adhesive onto a protective release layer (col. 2, lines 53-55), which becomes activated only upon the application of heat (col. 1, lines 43-45). Sawamura et al. employs a silicone-based adhesive to transfer labels to a silicone-rubber part. These references do not place a preformed self-adhesive stack into a mold; they do not use a silicone resin, nor do they adhere said silicone resin to the preformed self-adhesive stack using a silicone-based adhesive. Applicants contend that the above-mentioned references do not teach all of the elements of the present invention, and when viewed as a collective whole do not make the present invention obvious to one of ordinary skill.

Applicants process differs from the prior art in that a self-adhesive stack is placed in a mold followed by injection of a silicone resin, curing and then removing the self-adhesive molded silicone part from the mold assembly. The utilization of a preformed stack is markedly different from that method used by Strickland et al. As mentioned above, Strickland et al. introduced adhesive onto their protective layer by either casting or extruding (col. 2, lines 53-55), while Applicants place the preformed adhesive stack into the half-mold M1. Furthermore, the adhesive employed by Strickland et al. is absorbed (col. 1, lines 43-44) into the sole of the shoe. This adhesive is unlike the silicone-based adhesive used by Applicants. The only reference in Strickland et al. to "silicone" is as its role as a release liner (col. 2, line 17). Furthermore, the use of silicone resin is certainly unlike the extruded silicone-rubber parts taught by Gerritsen and Clark, and markedly different from the silicone liquid-injection-molded rubber used by Sawamura et al.

Both silicone resins and silicone rubbers, herein after referred to as resins and rubbers respectively, can be formed from chlorosilanes having the general formula  $R_xSiCl_{4-x}$ . The chlorosilanes ( $R_xSiCl_{4-x}$ ) may then be treated with water, i.e., hydrolyzed, to form siloxanes. An abbreviated representation of this process is as follows:



When  
 $x = 0$  or  $1$   
(highly branched siloxanes; **resins**)  
 $x = 2$   
(linear siloxanes; **rubber precursors**)

where the "highly branched siloxanes" are synonymous with resins and "linear siloxanes" are precursors of rubbers. (It should be noted that the representation above is only a partial schematic of the entire process as other processes and chemical reagents may be involved.) The difference in x-values (resins:  $x = 0$  or  $1$ ; rubber-precursors:  $x = 2$ ) means that upon the addition of water, the formed siloxanes have markedly different properties. When the x-

value equals 0 or 1 (i.e., for resins), the resultant siloxanes are highly branched oligomers whose average molecular weights are generally less than 10,000 g/mol. When the x-value equals 2 (i.e., for rubber-precursors), the resultant siloxanes are linear and give rise to polymers whose average molecular weights are typically greater than 500,000 g/mol. While there are many other differences to consider, these differences are beyond the scope of this discussion. Examiner is directed to a copy, attached as Appendix I, of a relevant section found in Kirk-Othmer's Encyclopedia of Chemical Technology (4<sup>th</sup> Edition; vol. 22, pp. 107 – 116, specifically pp. 112-113) for additional information. The most important point to note is that the silicone product used in the applied prior art is silicone rubber, while that used by Applicants is silicone resin.

Accordingly, the combined references do not teach or suggest all of the claimed elements, and Applicants respectfully request that the Examiner withdraw the rejection over Gerritsen (U.S. Patent 4,658,548), in view of Clark (U.S. Patent 4,351,686), Strickland et al. (U.S. Patent 5,983,527), and Sawamura et al. (EP 0878285A1).

The Examiner's rejection of the claimed method under 35 U.S.C. 103(a) as being obvious in light of Sawamura et al. (EP 0878285A1) and Dornbusch et al. (U.S. Patent 4,883,697) is obviated by way of amendment. Sawamura et al. uses a silicone-based adhesive to facilitate the transfer of designs to silicone-rubber parts, but does not produce self-adhesive parts. Dornbusch et al. is silent to the use of silicone products and to self-adhesive parts. Amending the claimed method defining the protective sheet as being removable distinguishes the current invention from these two prior art references, as agreed at the interview. Applicants respectfully request that the Examiner withdraw the rejection of the claimed method based on these two references.

Applicants submit that the present application is in a condition for allowance. Early notification to this effect is respectfully requested.

Respectfully submitted,

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VOLUME 22  
SILICON COMPOUNDS  
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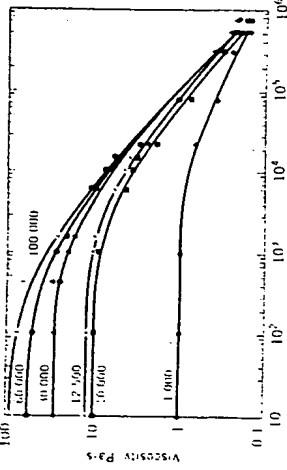


Fig. 5. Shear rate vs viscosity for PDMS. Numbers on curves indicate molecular weights. To convert Pa s to poise, multiply by 10.

surfaces to form films of molecular dimensions (344,345). This phenomenon is greatly affected by even small changes in the chemical structure of siloxane in the siloxane polymer. Increasing the size of the alkyl substituent from methyl to ethyl dramatically reduces the film-forming ability of the polymer (346). The phenyl-substituted silicones are spread onto water or solid surfaces more slowly than PDMS (347).

Dimethylsilicone polymers are often described as having a combination of silicene and paraffin structures, and the orientation of the polymer chains onto surfaces, physically, by chemical affinity, or bonding, can contribute to the observed surface properties. The surface tension of hexamethyldisiloxane,  $\text{MM}_6$ , is 15.7 mN/m ( $= \text{dyn/cm}$ ). Increasing incorporation of  $\text{MD}_4\text{M}$  increases the value to about 20 dyn/cm for higher viscosity fluids. Silicone fluids are characterized by their hydrophobicity (resistance to water), and the contact angle between PDMS and water is between 100° and 110°. Carefully deposited dimethylsiloxane on soda lime glass has a contact angle of about 60° at room temperature; the angle increases with increasing temperature (348).

Gases are soluble in dimethylsilicone polymers and PDMS is permeable to water vapor. The solubility of air, nitrogen, and carbon dioxide at 101.3 kPa (1 atm) is 0.17, 0.19, and 1.00  $\text{cm}^3/\text{cm}^3$ , respectively (348). About 250 to 300 ppb of water can dissolve in dimethylsiloxane at 25°C and 95% relative humidity (349). The water solubility of silanol-terminated oligomers increases with decreasing molecular weight, and the lowest monomer, dimethylsilanediol, is water-miscible. Silicone oils are soluble in nonpolar organic solvents such as benzene, toluene, dimethylether, chloroform, methyl ethyl ketone, methylene chloride, or kerosene. Incorporation of phenyl and especially trifluoropropyl or  $\beta$ -cyanoethyl functionality onto the polymer decreases the solubility of siloxane in organic solvents (342). They are slightly soluble in acetone, ethanol, and butanol, and relatively immiscible in methanol, ethylene glycol, and water. Exposure to strong acids or bases reequilibrates PDMS.

Silicone fluids have good dielectric properties, loss factor, specific resistance, and dielectric strength at normal operating conditions, and the properties vary only slightly with temperature (59,328,350). The properties in combination with relatively low flammability have led to the use of silicones in transformers and other large electrical applications (351). The dielectric constant of a 1000-cSt oil is 2.8 at 30°C and 2.6 at 100°C. The loss factor is low,  $1.2 \times 10^{-4}$  at 20°C, and behaves irregularly with frequency. Specific resistance is  $4 \times 10^{12}$  ohm-cm. The dielectric strength is 120 kV/cm (20°C, 50 cP, 6 kV/s).

Silicone oils are good hydrodynamic lubricants but have generally poor frictional lubricating properties (352,354). The latter can be improved by incorporating chlorophenyl groups into the polymer side chains (355). For steel on steel, the coefficient of friction is about 0.3–0.5. The load-bearing capacity of PDMS (Almen-Wickland machine) is only 50–150 kg, compared with 1000 kg for polychlorophenylmethylsiloxane and up to 2000 kg for mineral oil.

The thermal conductivity of dimethylsiloxane with viscosities  $> 100 \text{ mm}^2/\text{s}$  ( $\text{sl} = \text{cSt}$ ) is  $15.5 \text{ J}/(\text{m} \cdot \text{K})$  ( $3.7 \times 10^{-4} \text{ cal}/(\text{cm} \cdot ^\circ\text{C})$ ), and is roughly constant with increasing viscosity (356). The specific heat is  $1.55-1.70 \text{ J}/(\text{g} \cdot ^\circ\text{C})$  ( $0.17-0.41 \text{ cal}/(\text{g} \cdot ^\circ\text{C})$ ) over the 20–200°C range and is practically independent of viscosity (357). Thermal expansion of PDMS is  $-0.1\%/\text{ }^\circ\text{C}$  (356).

Liquid silicone oils are highly compressible and remain liquid over pressure ranges where normal paraffin oils have already solidified (358,359). This

property, combined with a wide temperature use range, is the reason for silicone use in a large number of hydraulic applications. The adiabatic compressibility of 1000-cSt dimethylsiloxane oils is  $-100 \text{ Pa}^{-1}$  ( $100 \text{ cm}^2/\text{dyn}$ ) and decreases slightly with increasing viscosity, similar to paraffin oils. PDMS oils can withstand pressures greater than 3.4 GPa (35,000 kg/cm<sup>2</sup>), even though they are compressed  $> 30\%$ .

Dimethylsilicone fluids are transparent to visible light and microwave but absorb ultraviolet radiation at wavelengths below 280 nm (360). Siloxanes absorb strongly in the infrared between 1000 and 1100  $\text{cm}^{-1}$  ( $\text{Si}-\text{O}$  stretching), 1300–1350  $\text{cm}^{-1}$  ( $\text{Si}-\text{C}$  stretching), and 2950–3000  $\text{cm}^{-1}$  ( $\text{C}-\text{H}$  stretching) (361). The speed of sound in PDMS is 347.3 m/s for a 100-cSt fluid at 30°C, and decreases with increasing temperature (362). Methylsilicone fluids are cross-linked when exposed to gamma ray or electron beam irradiation (363). Polymers containing aromatic substituents are more resistant than dimethylsiloxanes.

**Silicone Heat-Cured Rubber.** Silicone elastomers are made by vulcanizing high molecular weight ( $> 5 \times 10^6$  mol wt) linear polydimethylsiloxane polymer, often called gum. Fillers are used in these formulations to increase strength through reinforcement. Extending fillers and various additives, e.g., antioxidants, adhesion promoters, and pigments, can be used to obtain certain properties (59,357,364).

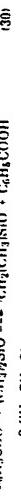
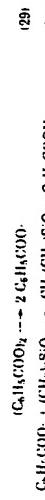
Peroxides are typical vulcanizing agents and the mechanism of cure involves

free-radical abstraction of a silicon methyl group proton and subsequent dimer-

ization of the methyl radicals to form ethylene cross-links (e.g., 29–41)(365,366).

Vinyl-containing polymers are often used to control the cross-linking reaction. Commonly used peroxides include di-*t*-butyl peroxide [110-05-4], benzoyl

peroxide [94-36-0], di(*p*-cumyl) peroxide, and di(*p*-chlorophenyl) peroxide. The choice of peroxide is made based on the desired cure temperature and rate. Table 5 lists some common peroxide curing agents, typical cure temperatures, and some recommended processing conditions.



Unlike natural rubber, silicone rubber does not stress-crystallize when elongated, which leads to relatively poor physical properties. Unfilled silicone rubber has only a 0.35 MPa (50 psi) tensile stress at break. To overcome this, silicone rubber is compounded with 10 to 25 wt % reinforcing fillers, typically fumed silica, to improve the final rubber product properties (268,270,271,367). Other common fillers include precipitated silica, titanium dioxide, calcium carbonate, magnesium oxide, and ferric oxide. Pigments and colorants are also used. The addition of fillers to the gum stock can result in structuring when stored, which decreases the workability of the material. To prevent structuring, the filler is often treated with agents such as hexamethyldisilane to reduce surface hydroxyl functionality or with the addition of processing aids such as silicone oils, diphenylsilanediol, or dimethylpinacoxysilane (267,368).

The processing methods for silicone rubber are similar to those used in the natural rubber industry (53,369-371). Polymer gum stock and fillers are compounded in a dough or Banbury-type mixer. Catalysts are added and additional compounding is completed on water-cooled roll mills. For small batches, the entire process can be carried out on a two-roll mill. Heat-cured silicone rubber is

commercially available as gum stock, reinforced gum, partially filled gum, uncatalyzed compounds, dispersions, and catalyzed compounds. The latter is ready for use without additional processing. Before being used, silicone rubber is often freshened, i.e., the compound is freshly worked on a rubber mill until it is a smooth continuous sheet. The freshening process eliminates the structuring problems associated with polymer-filler interactions.

It is common practice in the silicone rubber industry to prepare specific or custom mixtures of polymer, fillers, and cure catalysts for particular applications. The number of potential combinations is enormous. In general, the mixture is selected to achieve some special operating or processing requirement, and the formulations are classified accordingly. Table 6 lists some of the commercially important types.

Silicone rubber is most commonly fabricated by compression-molding-catalyzed gum stock at 100–180°C under 5.5–10.3 MPa (800–1500 psi) pressure. Mold release compounds are usually employed. Under these conditions the rubber is cured in a few minutes. Extrusion processing is used in the manufacture of tubes, rods, wire and cable insulation, and continuous profiles. Initial properties, so-called green strength, are obtained by curing in hot air or steam tunnels from 276 to 680 kPa (40–100 psi) at 300–450°C for several minutes. Final physical properties are achieved by post-curing in air or steam, typically for 30–90 minutes. When silicone rubber must be bonded to other surfaces, e.g., metals, plastics, or ceramics, primers are used. Silicate or titanate esters from the hydrolysis of tetraethylorthosilicate or tetraethyltinate are often used as primers. Silicone rubber-coated textiles and glass cloth are made by initially dissolving gum stock in solvent and applying the rubber by dip coating. The fabric is then dried and the rubber cured in heated towers. Tubes and hose can

Table 5. Cure Agents for Silicone Rubber\*

Curing agent	Commercial name	Temperature, °C	Property
di(2,4-dichlorobenzoyl) peroxide; benzoyl peroxide	Cadca 78-50 or Luperco CST Cadex RS or Luperco AST	104–132 116–138	hot-air vulcanizing molding, steam curing
dicumyl peroxide <sup>c</sup>	Di-CUP 40C	154–177	molding thick sections, bonding, steam curing
2,5-di( <i>t</i> -butylperoxy)-2,5-dimethylhexane <sup>d</sup>	Varox, Luperco 101XL, or Luperco 101 <sup>e</sup>	166–182	molding thick sections, bonding, steam curing

<sup>a</sup>Ref. 357.<sup>b</sup>50% active basic composition.<sup>c</sup>40% active powder composition.<sup>d</sup>50% active powder composition.<sup>e</sup>100% active liquid.

Table 6. Properties of Different Classes of Silicone Rubbers\*

Class	Hardness, durometer	Tensile strength, MN/m <sup>2</sup>	Elongation, %	Useful temperature range, °C	
				Tensile, min	Tensile, max
general purpose low modulus, room set	40–80 50–90	4.8–7.0 4.8–7.0	100–400 80–400	15–50 10–15	260 260
extreme low temperature wire and cable solvent-resistant high strength flame retardant	25–80 40–50	5.5–10.3 9.6–11.0	150–600 500–700	20–50 100–260	3–1 2.8–3.8

<sup>a</sup>Ref. 372–376.<sup>b</sup>To convert MPa to psi, multiply by 145.<sup>c</sup>At 150°C, 22 h.<sup>d</sup>To convert J/cm<sup>2</sup> to lb/in<sup>2</sup>, multiply by 57.1.

be formed on mandrels from this fabric into complex shapes. Foamed or sponge silicone rubber can be made by incorporating chemical blowing agents into the rubber stock, which eliminates typically nitrogen or carbon dioxide under the thermal curing conditions. Sponge silicone rubber made in this way has a closed cell structure and densities of 0.4–1.0 g/cm<sup>3</sup>.

Vulcanized silicone rubber is characterized by its wide temperature use range (−50 to >200°C), excellent electrical properties, and resistance to air oxidation and weathering conditions. Silicone rubber is also extremely permeable to gases and water vapor. The mechanical properties of silicone rubber are generally inferior to most organic (butyl) rubbers at room temperature. Tables 6, 7, and 8 list some typical physical properties for vulcanized silicone rubber. Silicone rubber can be made with varying degrees of hardness. Shore A values from 20 to 90 can be made; the best physical properties are obtained from 50 to 70. The properties of silicone change with temperature (376). The Young's modulus drops from 10<sup>5</sup> to 2 × 10<sup>4</sup> MPa (14.5 × 10<sup>4</sup> to 2.9 × 10<sup>3</sup> psi) from −50°C to room temperature and then is fairly constant to 260°C. Tensile strength at break decreases from 6.9 MPa (1000 psi) at 0°C to 2.1 MPa (300 psi) at 300°C. Typical elongation at break values range from 300 to 700%, depending on the composition.

The compression set of silicone rubber is similar to organic types of rubber at low (0–50°C) temperatures, ranging from 5 to 15% (380). Above 50°C, silicone

Table 7. Properties of Silicone Gums\*

Type	CAS Registry Number	Density, $\rho^{\text{m}}$ , g/cm <sup>3</sup>	Temperature, $T_e$ , °C	ASTM D926, Williams plasticity
(CH <sub>3</sub> ) <sub>2</sub> SiO	[90/6.0/6]	0.98	−123	95–125
CH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> )SiO	[90/5.12/3]	0.98	−113	135–180
CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> H <sub>2</sub> SiO)	[2579.149.3]	1.25	−65	

\*Ref. 331, 373–375.

Table 8. Permeability of Silicone Elastomers\*

Type	CAS Registry Number	Temperature, $T_e$	Gas	Permeability, $\text{nmol}/(\text{m} \cdot \text{s} \cdot \text{Pa})^b$
dimethyl silicone	[63148-62-9]	25	CO <sub>2</sub>	180
		25	O <sub>2</sub>	35
		25	air	19.6
		30	butane	0.49
		70	butane	0.76
		26	CO <sub>2</sub>	35
		26	O <sub>2</sub>	5.8
		31	CO <sub>2</sub>	105
		31	O <sub>2</sub>	17.8

\*Ref. 377–379.

<sup>b</sup>To convert  $\text{nmol}/(\text{m} \cdot \text{s} \cdot \text{Pa})$  to  $(\text{cm}^3 \text{ cm})/(\text{s} \cdot \text{cm}^2 \cdot \text{nm Hg})$ , multiply by  $3 \times 10^{-8}$ .<sup>c</sup>Methyl/trifluoropropyl silicones.Silicone rubber film is 10 to 20 times more permeable to gases and water vapor than organic rubber (380). The water permeability of silicone rubber is  $\sim 14 \times 10^{-6} \text{ mol}/(\text{m} \cdot \text{s} \cdot \text{Pa}) (1.2 \times 10^{-6} \text{ g}/(\text{m} \cdot \text{s}))$ , which means that silicone rubber can absorb about 35 mg of water per square centimeter of surface area after seven days exposure (377). Table 8 shows the permeability of silicone to common gases. Organic solvents can diffuse and swell into silicone rubber, significantly decreasing the physical properties of the material. The degree of swelling depends on the solubility parameters of the solvent and the rubber, as illustrated in Figure 6.Solvent-resistant rubber based on either trifluoropropylmethylsiloxane or  $\beta$ -cyanoethylmethylsiloxane has been developed for applications, e.g., as fuel tank sealants, where the material will be exposed to aggressive solvents. Those based on trifluoropropylmethylsiloxane are more important commercially. Pure water has little effect on silicone; however, long exposures in the presence of acid or

Table 9. Electrical Properties of Typical Silicone Rubber\*

Property	Value
volumetric resistivity <sup>a</sup> , $\Omega \cdot \text{cm}$	$1 \times 10^{10}$ – $1 \times 10^{18}$
electric strength, $V/25.4 \mu\text{m}$ ( $\approx V/\text{mil}$ )	400–700
dielectric constant, 60 Hz	2.95–4.00
power factor, 60 Hz	0.001–0.01
surface resistance, $\Omega$	$3.0 \times 10^3$ – $4.5 \times 10^4$
dielectric loss factor, $\tan \delta$	$5 \times 10^{-4}$ – $10^{-3}$

\*Ref. 35.

†Ref. 56.

Silicone rubber film is 10 to 20 times more permeable to gases and water vapor than organic rubber (380). The water permeability of silicone rubber is  $\sim 14 \times 10^{-6} \text{ mol}/(\text{m} \cdot \text{s} \cdot \text{Pa}) (1.2 \times 10^{-6} \text{ g}/(\text{m} \cdot \text{s}))$ , which means that silicone rubber can absorb about 35 mg of water per square centimeter of surface area after seven days exposure (377). Table 8 shows the permeability of silicone to common gases. Organic solvents can diffuse and swell into silicone rubber, significantly decreasing the physical properties of the material. The degree of swelling depends on the solubility parameters of the solvent and the rubber, as illustrated in Figure 6.

Solvent-resistant rubber based on either trifluoropropylmethylsiloxane or  $\beta$ -cyanoethylmethylsiloxane has been developed for applications, e.g., as fuel tank sealants, where the material will be exposed to aggressive solvents. Those based on trifluoropropylmethylsiloxane are more important commercially. Pure water has little effect on silicone; however, long exposures in the presence of acid or

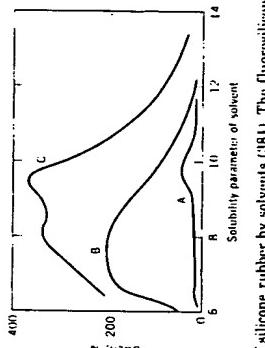


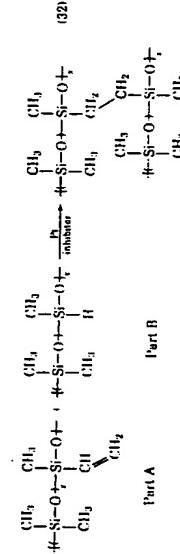
Fig. 6. Solubility of silicone rubber by solvents (381). The fluorosilicones (A) are methylphenylsilicones.

Inse catalyst causes degradation and reversion of the rubber to a sticky gum (376,382). Prolonged exposure to temperatures above 300°C. in air causes the rubber to stiffen and ultimately to become brittle (376). As with silicone oil, the principal chemical pathways of degradation are retrocyclization and oxidation of the polymer alkyl groups. Heating in air at 125°C causes a decrease in elongation and an increase in hardness, but no important changes in tensile properties are observed.

**Silicone rubber**. Silicone rubber burns with a high char yield, and the residual material is nonconducting silicon dioxide. The limiting oxygen index for a typical rubber formulation is about 20. Flame-retardant versions are available with oxygen index values as great as 40–50 (372). In general, silicone rubber is not resistant to gamma or electron beam radiation and undergoes cross-linking, which leads to embrittlement (383). Increasing levels of phenyl-containing silicone in the rubber improves the radiation resistance (384).

**Silicone Liquid-Injection-Molding Rubber.** An increasingly important cured rubber, which is typically compression-molded from high viscosity gum stock liquid-injection-molded LIM rubber is made from low viscosity starting materials, 1000–2000 mPa·s<sup>0.5</sup> (371), and is cured in molds similar to those used for plastic injection molding. The principal advantages of LIM include rapid cycle times and the ability to fill complex mold shapes because of the low viscosity of the inputs. Rubber parts can be cured in 10–40 s using low molding pressures, ca. 2–20 MPa (300–3000 psi), and low curing temperatures, typically 150–260°C. (345). LIM processing is being increasingly used for applications such as electrical connectors, O-ring seals, valves, electrical components, health care products, and sporting equipment such as goggles and scuba masks.

Silicone LIM rubber is made from a two-component polymer system. One part (Part A) contains a linear polydimethylsiloxane polymer with pendant Si—H functionality, reinforcing fillers such as fumed silica, extending fillers, pigments, and stabilizers. The second part (Part B) contains linear polydimethylsiloxane with terminal and pendant vinyl groups, reinforcing and extending fillers, a platinum hydrosilylation catalyst, and a catalyst inhibitor, commonly olefin, amine, or phosphine ligands. After mixing and heating, the catalyst initiates the cross-linking reaction by addition of the Si—H group to the double bond (eq. 32). Latent cure catalysts have been developed that allow the formulation of one-component products (346). These systems work by incorporation of platinum ligands that deactivate the hydrosilylation catalysts at room temperature; however, when heated to temperatures above 100°C, these catalysts become active.



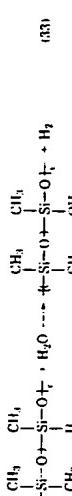
Inse catalyst causes degradation and reversion of the rubber to a sticky gum

(376,382). Prolonged exposure to temperatures above 300°C. in air causes the rubber to stiffen and ultimately to become brittle (376). As with silicone oil, the principal chemical pathways of degradation are retrocyclization and oxidation of the polymer alkyl groups. Heating in air at 125°C causes a decrease in elongation and an increase in hardness, but no important changes in tensile properties are observed.

**Foam Rubber.** Flexible foamed silicone rubber can be fabricated with physical properties equivalent to heat-cured rubber (385). Shore A hardness can range from 30 to 70, depending on formulations. Typical physical properties include tensile strengths as high as 9.7 MPa (1400 psi), 500–775% elongation at break, and tear strength of >30 N/mm (180 lb/in.). Compression sets of less than 10% can be achieved if the material is baked after processing.

**Foam Rubber.** Flexible foamed silicone rubber can be fabricated with a flame retardancy greatly superior to that of the urethane-type foam. A soft, blowing, low to medium density (40–240 kg/cm<sup>3</sup>/5–15 lb/ft<sup>3</sup>) silicone framed rubber can be prepared using polymers similar to those used in LIM products (387–390). Two components are mixed at room temperature; one part is pendant SiH containing polydimethylsiloxane and fillers, and the other consists of terminal and pendant vinyl containing PDMS, reinforcing and extending fillers, a platinum hydrosilylation catalyst and inhibitor, water, alcohol, and an emulsifying agent. Typical time for foam formation is 20 min.

Two chemical reactions occur simultaneously when mixed. One is the platinum-catalyzed reaction of hydroxyl groups from water or alcohol with poly-SiH to give hydrogen gas (eq. 33). This reaction is the source of the blowing agent that forms the foam. The second reaction is the cross-linking of SiI and Si—Vinyl, which increases the polymer viscosity and ultimately gels and cures to give an elastomer. This is the same cross-linking reaction depicted in equation 32. Proper control of the kinetics of these two reactions is critical to achieving a foam having good physical properties.



Silicone foam thus formed has an open cell structure and is a relatively poor insulating material. Cell size can be controlled by the selection of fillers, which serve as bubble nucleating sites. The addition of quartz as a filler greatly improves the flame retardancy of the foam; char yields of >65% can be achieved. Because of its excellent flammability characteristics, silicone foam is used in building and construction fire-stop systems and as pipe insulation in power plants. Typical physical properties of silicone foam are listed in Table 10.

**Silicone Resins.** Silicone resins are an unusual class of organosiloxane polymers. Unlike linear polysiloxanes, the typical silicone resin has a highly branched molecular structure. The most unique, and perhaps most useful, characteristics of these materials are their solubility in organic solvents and apparent miscibility in other polymers, including silicones. The incompatibility between solubility and three-dimensional structure is caused by low molecular weight ( $M_n < 10,000$  g/mol) and broad polydispersity of most silicone resins.

A wide variety of organosilicone resins containing a combination of M, D, T, and/or Q groups have been prepared and many are commercially manufactured. In addition, resins containing hydrosilylation-reactive SiH and SiVi groups, or other functionalities, including OH and phenyl groups, are known. Two classes of silicone resins are most widely used in the silicone industry: MQ and TD resins.

Table 10. Physical and Flammability Properties of Silicone Foam Rubber\*

Property	Value
density, kg/m <sup>3</sup>	80–240
tensile strength, MPa <sup>b</sup>	0.52
elongation, %	90
thermal conductivity, W/m·K	0.06
operating temperature range, °C	-60 to 205
limiting oxygen index	30
UL-94 flammability (3.2-mm thick)	V-0
flame spread index (ASTM E662)	16
smoke density flanking (ASTM E662)	18
smoke density smoldering (ASTM E662)	9
verticible burn (FAA 25.853)	compliant

<sup>a</sup>Ref. 391<sup>b</sup>To convert MPa to psi, multiply by 145.

**MQ Resins.** These resins are composed of clusters of quadrafunctional silicate Q groups end-capped with monofunctional trimethylsiloxy M groups. The structure of an MQ resin molecule is defined by three characterization parameters: M/Q ratio, % molecular weight, and % OH. Standard analytical techniques have been used to quantify these parameters, including <sup>29</sup>Si-nmr to determine M/Q, ratin, gpc for molecular weight, and far for % OH (392,393). Most commercially useful MQ resins have an M/Q ratio between 0.6 and 1. Ratios lower than 0.6 result in insoluble solids, whereas those greater than 1 produce liquids (394). Molecular weight is related to M/Q ratio; higher molecular weights are  $M_n = 10,000 \text{ g/mol}$  for an M/Q of (393,394). The silanol content (% OH by weight) of these resins, typically ranging between 0 and 3%, is process-dependent (Fig. 7). An ir study indicates that OH groups are intramolecularly associated through hydrogen bonding (394). A computer-generated molecular structure of a common commercially prepared MQ resin

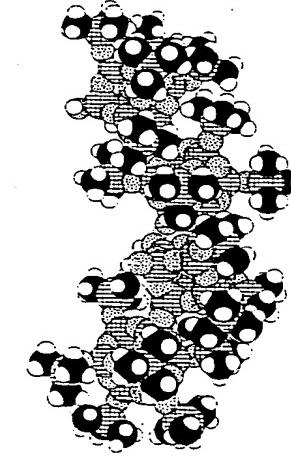
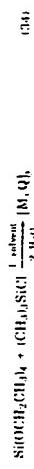


Fig. 7. Molecular structure of a typical MQ resin, [M<sub>0.67</sub>O<sub>0.11</sub>SiO<sub>3.33</sub>]<sub>n</sub>, where O = II, ● = C, ○ = Si, and ⊖ = O.

has been reported (393). This structure, shown in Figure 7, consists of a chain of silicate clusters end-capped with trimethylsiloxy groups.

MQ resins are commercially manufactured by one of two processes: the ethyl silicate or the sodium silicate process. In the ethyl silicate process, these resins were first prepared by hydrolysis of tetrachlorosilane and trimethylchlorosilane in the presence of an aromatic solvent (eq. 34). This process is versatile and reproducible; it can be used to prepare soluble MQ resins with M/Q ratios ranging between 0.6 and 4. The products of these reactions typically contain high levels of residual alkoxy silane groups.



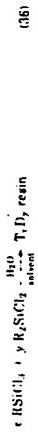
A more economical route to MQ resin uses low cost sodium silicate and trimethylchlorosilane as inputs (eq. 35) (395). The sodium silicate process is initiated by acidifying an aqueous sodium silicate solution to a pH of 2. The resulting hydrosol quickly builds molecular weight. The rate of this increase is moderated by the addition of an alcohol such as 2-propanol. The hydrosol is subsequently silylated by the addition of trimethylchlorosilane. This process, which is kinetically sensitive and limited to synthesizing M/Q ratios of 1 or less, is preferred when MQ resins having high (> 1%) OH content are required (395).



Both the ethyl and sodium silicate processes can be modified by substituting SiH<sub>4</sub> or SiVi-functional chlorotitanates or combinations of chlorosilanes to produce hydrosilicon-reactive MQ resins (396,397).

The most prominent use of MQ resins is as the tackifying agent for silicone pressure-sensitive adhesives (PSA) (398,399). The other main component of silicone PSA is a silicone gum. This mixture of MQ resin and silicone gum is applied to a tape backing such as polyethylene/terephthalate (PET) or polyethylene/terephthalate (PET) and cured in the presence of a peroxide catalyst to provide an adhesive tape. MQ resins are also commonly used as control-release additives for silicone paper release products, as reinforcing fillers for liquid-injection-moldable silicones, in masonry sealants, and in leather/textile water-repellent coatings (398,400–404). Additional uses of MQ resins are as surfactants. MQ resins are commercially attractive for use in defoaming applications as well as for stabilizing frothed urethane for high density carpet bucking. Virtually every use for MQ resins is as a blend with a polydimethylsiloxane. These blends have been characterized as interpenetrating networks (402,405,406). MQ resin/PDMS blends are microphase-separated. One phase is PDMS-rich and has a glass-transition temperature of 107°C. Thus  $T_g$  does not change with changes in the blend ratio. The other phase is an MQ resin/PDMS-miscible phase whose  $T_g$  varies linearly from –100° to 200°C as the composition of the blend is changed from 30 to 90% MQ resin (394). These unique viscoelastic properties contribute to the versatility of silicone products containing MQ resin.

**TD Rosins.** The other important class of silicone resins is TD resins. These materials are simply prepared by cohydrolyzing mixtures of chlorosilanes in organic solvents (eq. 36), where R = CH<sub>3</sub> or C<sub>6</sub>H<sub>5</sub> (407).



A variety of liquid and solid resins can be prepared by varying the T/D ratio. Commercial TD resins are available, containing from 5 to 85% T groups. Mixtures of methyl and phenylchlorosilanes are also frequently used. Some TD resins are modified by the addition of catalysts to reduce the silanol content, thereby increasing the molecular weight. Contrary to MQ resins, which are very soluble, TD resins are unstable toward silanol condensation reactions.

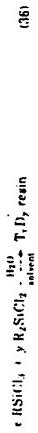
TD resins are used as protective coatings, electrical coatings, sealants, laminates, and water repellents (55). TD resins are also useful in high performance paints. Compositions high in silanol content are utilized in reactive formulations. Low silanol TD resins are used as reactive additive to alkynil paint formulations. Attractive features of TD resin-based protective coatings include superior, uv-resistant, weatherability and excellent high and low temperature properties. Silicone electrical coatings are preferred when good dielectric insulation is required over a broad temperature range. TD resins are also used to saturate glass or Kevlar fabrics. After curing, these flexible compositions are used in a variety of applications. TD resin-based water repellents are used chiefly with siliceous substrates. Some typical TD silicone resin properties are as follows: dielectric strength = 68,000 V/mm; dielectric constant = 2.9 at 60 Hz and 25°C; dissipation factor ~ 0.006 at 60 Hz and 25°C; surface resistivity =  $1 \times 10^4$  J/cm<sup>2</sup>; and volume resistivity =  $1 \times 10^{14}$  Ω·cm.

**Organosilicone Coating Products:** Silicone products are used in a large variety of coating applications; most prominent among these are silicone pressure-sensitive adhesives (PSAs), plastic hardcoats, and paper release coatings (398,399).

**Pressure-Sensitive Adhesives.** Silicone PSAs are used primarily in specialty tape applications that require the superior properties of silicones, including resistance to harsh chemical environments and temperature extremes (398,399). Silicone PSAs are also used in applications requiring long service life, electrical insulation, and protection from moisture. Another distinctive advantage of silicone PSAs is their ability to wet low surface energy tape substrates such as PTFE.

Silicone PSAs are blends or interpenetrating networks (IPNs) composed of a tackifying MQ resin cured in a cross-linked polysiloxane network. The synthesis and structure of MQ resins have been described above. The poly(siloxane) network is traditionally derived by free-radical cross-linking of a high molecular weight TDMS polymer or gum using a peroxide catalyst, such as benzoyl peroxide or 2,4-dichlorobenzoyl peroxide. The curing reaction is performed immediately after the PSA has been coated onto a tape substrate, such as PET, PTFE, or Kapton. Uncured PSAs are supplied as a solution in an organic solvent. Some silicone PSAs also incorporate phenyl groups onto the gum portion of the adhesive to increase the tack temperature.

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Another important aspect of the chemistry of silicone PSAs is the molecular interaction between the tackifying MQ resin and the PDMS network. For optimal adhesive properties, it is important that some covalent bonding exists between the resin and the PDMS. This bonding is usually achieved by promoting a silanol condensation reaction between residual OH groups on the resin and on the end caps of the PDMS. The condensation reaction can occur either during blending of the PSA components or during processing of the tape. Studies of the viscoelastic properties of cured silicone PSAs indicate that these materials are microphase-separated (394,405,406). The adhesive properties of PSAs are a function of the unique rheological properties of the MQ resin/PDMS blends.

The key adhesive properties of a silicone PSA are: tack, peel adhesion, and cohesive strength (lap shear). The required balance of these properties is controlled by several factors. A PSA composition rich in MQ resin usually favors low tack and high peel adhesion and cohesive strength values. A high cross-link density or a larger number of covalent bonds between the MQ resin and the PDMS network favors high cohesive strength at the expense of tack and peel adhesion. Low peel adhesion is observed when uncured cyclic or linear siloxanes are present. Other PSA properties important to the tape manufacturer, ie, viscosity, solvent content, cure time, and temperature, are typically controlled by varying the type and amount of organic solvent and peroxide cure catalyst. Primers are also frequently used to promote adhesion of the PSA to the tape bucking.

One advance in silicone PSA chemistry is the use of Pt-catalyzed hydrosilylation reactions as the method of cure (408). Advantages of hydrosilylation-cured silicone PSAs include lowering the level of solvent, lowering cure temperatures, increasing line speeds, as well as the ability to be used with a broader range of tape bucklings. In this technology, lower molecular weight polymers containing hydrosilylation-reactive SiH and SiVi groups are substituted for the traditional OI-end-capped PDMS gum. A Pt catalyst and inhibitor are used instead of a peroxide.

There are several important, specialized applications for silicone PSA tapes. Printers tapes mask selected areas of parts during etching or plating operations. Masking tapes are also used as protective coatings against high temperatures, radiation, harsh chemical environments, or moisture. These tapes are used frequently in the manufacture of printed circuit boards (410). Splicing tapes are used to join plastic films. Silicone PSAs are often used to splice low surface energy materials or to provide high cohesive strengths at temperature extremes. Plasma or flame spray tapes are used to protect selected metal surfaces during sandblasting or flame spraying operations. Silicone PSAs are particularly useful as the adhesive for electrical insulating tapes. A common application is as a wire wrap in motor coils. Silicone PSAs are also used in medical applications, notably as an adhesive for bandages and transformable drug delivery systems (410).

**Silicone Hardcoats.** Silicone hardcoat technology evolved from the need to develop thin film coatings to impart abrasion and chemical resistance to plastic substrates. The first commercial silicone hardcoat products were developed in the 1970s (411–413). The basic chemistry involves first hydrolyzing a trialkoxysilane in the presence of an aqueous colloidal silanol solution. The resulting solution is then diluted with alcohols such as isopropanol or n-butanol and